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Effect of the void formation on the explosive fracture of electron irradiated NaCl crystals

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Abstract

Experimental and theoretical results are presented on formation of colloids, halogen bubbles and large vacancy voids in heavily irradiated NaCl crystals leading to their explosive decomposition into small pieces under further irradiation or subsequent heating. The dependence of the radiation stability of material with increasing irradiation dose on the void evolution is analyzed. It is shown that voids can grow very fast as compared to colloids and bubbles. For doses higher than 100 Grad, the void dimensions can exceed the mean distance, first, between bubbles and then between colloids resulting in their collisions with voids. Collisions with bubbles fill the voids with gas, and subsequent collisions with colloids (during further irradiation or heating) bring the halogen gas and metal to a back reaction inside the voids. Such a sudden release of stored energy can be shown to result in a temperature spike (above 10^4 K) and instantaneous gas pressure rise up to 1 GPa within the voids, which may transform voids into penny-shaped cracks along the cleavage planes of the matrix. A subsequent growth of the cracks results in fracture of the material. Dependence of the critical amount of stored energy required for the void–crack transition on the mean size of the voids is estimated and compared with experimental data.

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Keywords: Radiation damage; Stored energy; Colloids; Bubbles; Voids; Fracture

1. Introduction

In the companion paper [1], the formation of large vacancy voids under electron irradiation of NaCl crystals observed in our recent experiments [2,3] is explained within a framework of a theoretical model, which is based on a new mechanism of dislocation climb [4]. The mechanism involves the production of V_F centers (self-trapped hole neighboring a cation vacancy) as a result of the absorption of excess H centers (halide interstitial ion with a trapped hole) at dislocation lines. Voids are shown to arise due to formation of vacancy pairs (two adjacent vacancies, one in the cation and one in the anion sub-lattice) in the reaction between F centers (vacancy in the halide sub-lattice with a

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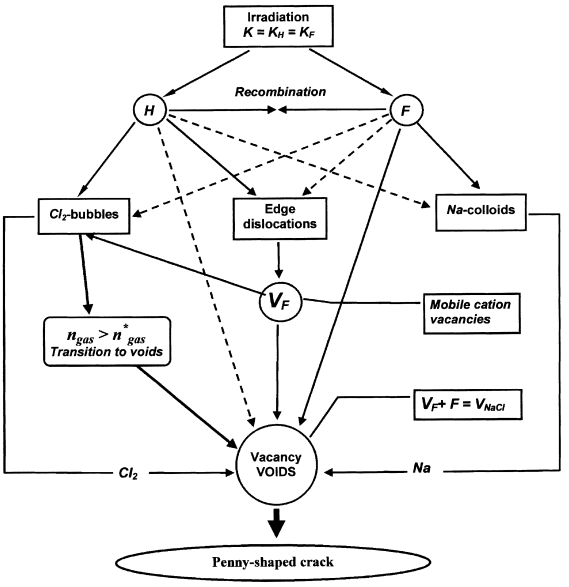

Fig. 1. Diagram of radiation-induced reactions between point defects (H- and F-centers, and cation vacancies) and extended defects (bubbles, dislocations and colloids) resulting in the void formation. Release of stored energy due to absorption of chlorine bubbles and sodium colloids induce the void–crack transition and a subsequent fracture of crystal.

trapped electron) and V_F centers at the surface of halogen bubbles.

Fig. 1 illustrates the radiation-induced reactions between point defects (PD) and extended defects (ED) based on the present model. Primary radiation-induced PD, namely, H and F centers, separate ultimately into bubbles, dislocations and metal colloids, which results in production of the secondary PD (cation vacancies) and ED (vacancy voids). It is shown that voids grow very fast as compared to colloids and bubbles (Fig. 5(c) in [1]). For doses higher than 100 Grad, the void dimensions can exceed the mean distance, first, between bubbles and then between colloids resulting in their collisions with voids. These collisions change the void evolution drastically, which is described in the present paper.

2. Explosion driven void–crack transition

According to the present model, chlorine bubbles (3–4 nm in size) are the most finely dispersed ED in the system (the inter-bubble spacing is typically below 10 nm [1]) so that they start to collide with growing voids first, filling them with chlorine gas. The chlorine in "bubbles" is in a solid or fluid state due to a super high pressure (in the GPa range) [5], but after collision with a void it becomes a gas. One can estimate the number of chlorine atoms, n_{Cl}, captured by a void of radius R_{V} as a product of the void volume and the bubble volume fraction, V_{B}, divided by the chlorine atomic volume, ω_{Cl}:

$$n_{\mathrm{Cl}} = \frac{4\pi}{3} R_{\mathrm{V}}^3 \frac{V_{\mathrm{B}}}{\omega_{\mathrm{Cl}}}. \tag{1}$$

The bubble volume fraction grows with irradiation dose at the same rate as the colloid volume fraction, $V_{\mathrm{C}} = (\omega/\omega_{\mathrm{Cl}})V_{\mathrm{B}}$, due to the balance between sodium and chlorine atoms stored in the unit volume of the matrix, where ω is the atomic volume of NaCl. Accordingly, the gas pressure in the voids (where it is in molecular form) is also determined by the colloid volume fraction,

$$P = \frac{(n_{\mathrm{Cl}}/2)kT}{(4\pi/3)R_{\mathrm{V}}^3} = \frac{kT}{2\omega_{\mathrm{Cl}}} V_B = \frac{kT}{2\omega} V_{\mathrm{C}}, \tag{2}$$

where we have used the equation of state of an ideal gas, which is valid in this pressure region. An estimate done for 100°C shows that even at maximum values of $V_{\mathrm{C}} \approx 10\%$, the pressure is 5×10^{-3} Gpa (50 atm), which is still lower than the surface tension of a void as large as 200 nm. So this pressure does not affect the void bias, which controls the void diffusion growth [1]. However, the chlorine accumulation in voids provides a very important possibility for the explosive back reaction with metallic sodium when a growing void hits the first colloid. The amount of released energy in this reaction is proportional to the energy released due to formation of one NaCl molecule, q_{NaCl}, and to the number of molecules formed as a result of collision, n_{NaCl}. The latter is equal to the mean number of sodium atoms in a colloid, which is close to the number of chlorine atoms accumulated in the void at the time of the collision (Fig. 2). The released energy heats up the reaction products inside the void resulting in an instantaneous tem-

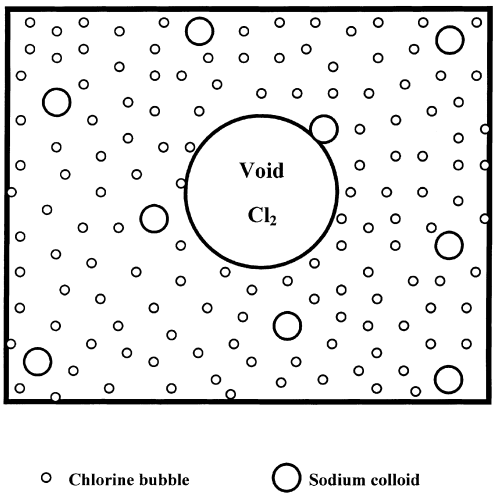

Fig. 2. Illustration of the distribution of chlorine bubbles, sodium colloids and voids in irradiated NaCl crystals. The void size is about the mean inter-colloid size, R_{expl}, when the first collision with a colloid is expected.

perature and pressure increase, which can be estimated as

$$\Delta T = \frac{q_{NaCl} n_{NaCl}}{C_P n_{NaCl}} = \left| C_P = \frac{5}{2}k \right| = \frac{2}{5}\frac{q_{NaCl}}{k} = 2 \times 10^4 \text{ K}, \quad (3)$$

$$\Delta P = \frac{n_{NaCl} k \Delta T}{(4\pi/3)R_V^3} = \left| n_{NaCl} = \frac{4\pi}{3} R_V^3 \frac{V_C}{\omega} \right| = \frac{2}{5}\frac{q_{NaCl}}{\omega} V_C \approx \mu V_C, \quad (4)$$

where C_P is the specific heat capacity of NaCl per molecule estimated as that for molecular ideal gas, which is equal to $5k/2$ in the case of diatomic molecules. The mean number of sodium atoms in a colloid at the time of the first collision with a void, n_{NaCl}, in Eq. (4) is expressed through the colloid volume fraction and void radius due to the condition of the first collision: $N_C(4\pi/3)R_V^3 = 1$. So the pressure increase due to the back reaction is proportional to the colloid volume fraction or, equivalently, to the amount of stored energy per unit volume. The proportionality coefficient is close to the matrix shear modulus μ, which is about 12 Gpa in NaCl. Such an increase of pressure may initiate a crack propagation from the void along the matrix cleavage plane (1 0 0) if it is bigger than some threshold value [6]: $P_{th} = \sigma_f/2$, where σ_f is the fracture stress corresponding to the Griffith crack,

$$\sigma_f = \sqrt{2\gamma E/\pi R_V}. \quad (5)$$

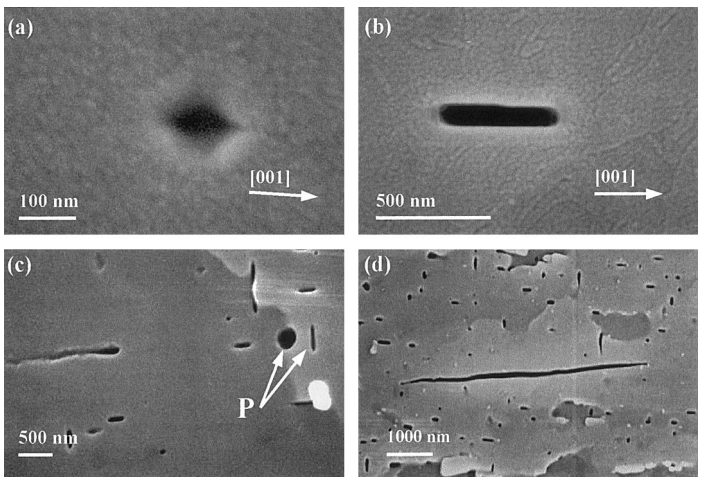

Fig. 3. SEM micrographs showing vacancy voids and cracks in natural rock salt crystals irradiated with 0.5 MeV electrons. (a) Equiaxial void at high resolution after irradiation to 60 Grad; latent heat of melting (LHM) of metallic Na is 0.45 J/g. (b) "Penny-shaped" crack formed after irradiation to 300 Grad, LHM of metallic Na is 0.8 J/g. (c) "Penny-shaped" voids/cracks in natural rock salt irradiated up to 300 Grad; LHM of metallic Na is 1.2 J/g. Two adjacent voids with different orientations are shown by the letter "*P*" with the arrows. (d) Long crack formed after irradiation to 300 Grad, LHM of metallic Na is 2.5 J/g.

The initial crack length in Eq. (5) is assumed to be about the void radius, R_V (Fig. 3(a)), which allows us to express the threshold colloid volume fraction, V_{th}, required to initiate the explosive crack propagation through the void size,

$$V_{th} = \frac{5\omega}{4q_{NaCl}}\sigma_f \propto R_V^{-1/2}. \quad (6)$$

The pressure and temperature spike is extremely short (in the picosecond range), which restricts the crack propagation distance to about 100 nm and results in the transition of an equiaxial void into a penny-shaped crack. This is illustrated in Figs. 3 and 4 showing the void–crack evolution with increasing irradiation dose and the amount of stored energy in crystals with different dopants. It is seen that the crack length increases gradually, which can be explained by a combined mechanism of diffusion accumulation and explosive release of energy in voids and cracks.

Ultimately, the diffusion plus explosion driven crack growth results in their coalescence (Fig. 3(d)) followed by fracture of the material into small pieces. The explosive fracture of irradiated samples can be also induced by their subsequent heating to temperatures of about 200°C as shown in Fig. 5(a). In this case, it is possible to carefully control the amount of stored energy by measuring the latent heat of melting (LHM) of Na before and after the fracture (Fig. 5(b)). The LHM decrease

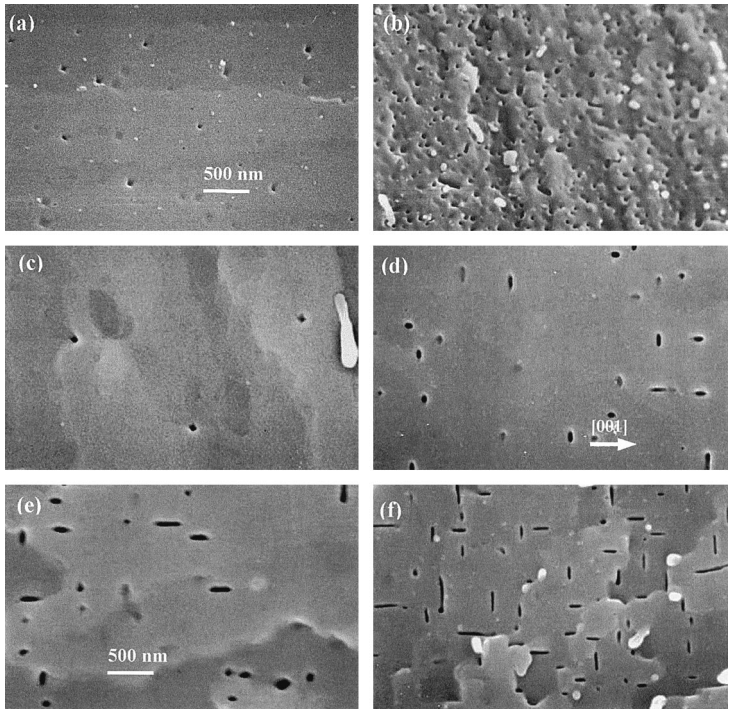

Fig. 4. SEM micrographs showing vacancy voids and cracks in $NaCl + KBF_4$ (0.03 mol%) (a, b) and in NaCl + K (0.1 mol%) (c–f) irradiated to different doses with 0.5 MeV electrons. $NaCl + KBF_4$: (a) Equiaxial voids formed after irradiation to 300 Grad, LHM of metallic Na is 2.1 J/g. (b) High density of equiaxial voids and sparse "Penny-shaped" cracks formed after irradiation to 300 Grad, LHM of metallic Na is 5.6 J/g. NaCl + K: (c) Equiaxial voids formed after irradiation to 60 Grad, LHM of metallic Na is 0.84 J/g. (d) Equiaxial voids and "Penny-shaped" cracks formed after irradiation to 90 Grad, LHM of metallic Na is 1.15 J/g. (e) Equiaxial voids and "Penny-shaped" cracks formed after irradiation to 180 Grad, LHM of metallic Na is 1.9 J/g. (f) High density of "penny-shaped" cracks formed after irradiation to 240 Grad, LHM of metallic Na is 2.9 J/g.

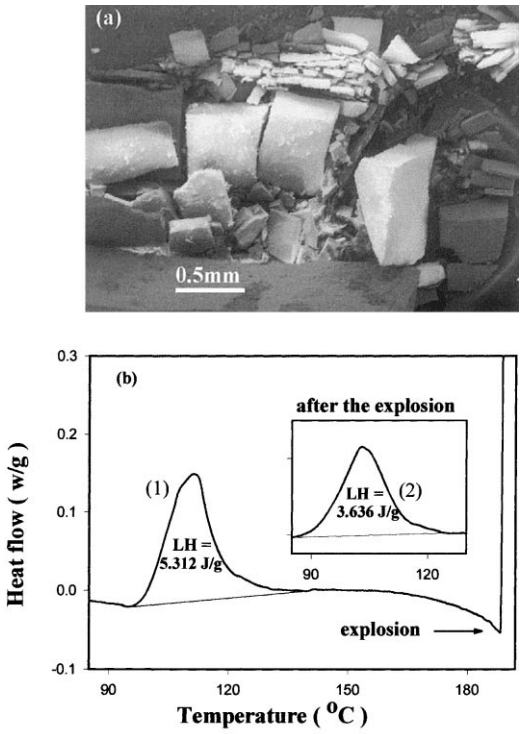

Fig. 5. Heating-induced explosion fracture of NaCl + K (0.1 mol%) samples irradiated with 0.5 MeV electrons to 300 Grad: (a) SEM micrograph of the exploded sample revealing large fragments and dust-like particles. (b) Differential scanning calorimetry (DSC) measurements of the LHM of metallic Na before (1) and after (2) the explosion at 189°C. The LHM has decreased by 32% due to the back reaction.

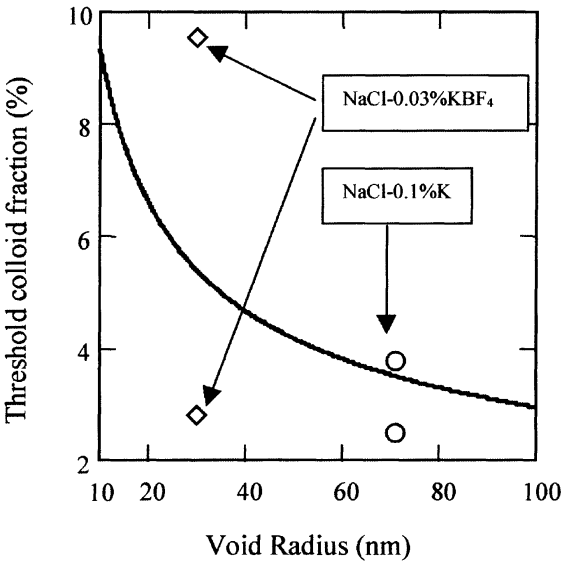

Fig. 6. A certain threshold colloid volume fraction, V_{th} (6) is required to initiate the explosive crack propagation. In this figure we have plotted V_{th} as a function of the radius of the equiaxial voids. Experimental points below the theoretical curve correspond to the situation in Fig. 4(a) and (c), in which only equiaxial voids can be seen, while those above the curve correspond to Fig. 4(b) and (d), in which the equiaxial voids coexist with penny-shaped cracks indicating the beginning of the void–crack transition.

after the fracture confirms that the latter was indeed due to the release of radiation-induced stored energy.

Comparison of pictures in Fig. 4 shows that the critical amount of stored energy initiating the formation of penny-shaped cracks (which may be called the *radiation fracture toughness*) is substantially higher in crystals doped with KBF_4 than in those dopes with potassium. According to Eq. (6), the radiation fracture toughness decreases with increasing void size as shown in Fig. 6, which is in agreement with experimental data shown in the same figure. Voids in crystals doped with KBF_4 are smaller than in those doped with K, which delays their transition to cracks to a higher level of stored energy. Note that the maximum void size does not increase with the irradiation dose since it is determined roughly by the inter-colloid spacing R_{expl} (Fig. 2). Indeed, the explosions that do not result in the void-crack transition (below the curve in Fig. 6) result in the void shrinkage due to the condensation of NaCl molecules at the void surface after the cooling down of the spike. So R_{expl} is a point of accumulation of voids in the size space until the critical amount of stored energy is reached, which depends on the kinetics of colloid formation affected by the dopants.

3. Summary

1. Small halogen bubbles formed in irradiated NaCl as a result of radiolytic process give rise to vacancy voids due to recombination of F and V_F centers at their surfaces after accumu-

lation of some critical number of halogen atoms.
2. Voids grow fast as compared to bubbles and metallic colloids eventually absorbing them, which brings the halogen gas and metal to a back exothermic reaction (explosion) inside the voids.
3. The explosion-induced gas pressure increase is proportional to the amount of stored energy per unit volume of the matrix. It may initiate the void–crack transition after the critical amount of stored energy is reached, which is determined by the void size.
4. A new (diffusion plus explosion driven) mechanism of crack growth is proposed. This mechanism may be a driving force of the explosive fracture of heavily irradiated crystals.

Acknowledgements

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